

THE OXIDATIVE REACTIVITY OF COAL CHARs IN RELATION TO THEIR STRUCTURE

by

M-L Chan*, J. M. Jones, M. Pourkashanian, and A. Williams

Department of Fuel and Energy, The University of Leeds,
Leeds, West Yorkshire, UK, LS2 9JT

*British Gas Research Centre, Ashby Road, Loughborough.

Keywords: coal, porosity, reactivity

Abstract: In the oxidation of highly porous carbons, the internal surface area can increase as a function of conversion due to pore growth and the opening up of sealed internal pores or cavities. Consequently, rate expressions for carbon oxidation are more accurately described in terms of the intrinsic reactivity, where differences in surface area and porosity are accounted for.

The oxidative reactivity of coal chars is complicated by a number of different factors which are explored in this paper. These include (i) the development of the pore structure during devolatilisation of the coal, (ii) the ash content and its distribution in the carbon matrix, (iii) the H and N functional groups present on the solid matrix, and the interrelation with volatile species present, (iv) the graphitic nature of the carbon surface and, the active surface area available for reaction.

Introduction

Coal char structure is influenced, not only by coal properties, but also by the temperature-time history which the coal particles experience within the combustor, i.e. heating rate, maximum temperature experienced, residence time at this temperature, and the gaseous atmosphere. This is because these variables, together with coal properties all influence the amount and nature of the volatile, as well as their rate of release. These factors determine both the macroscopic morphology and the microscopic porosity of the resultant char. The porosity is particularly important because it can control the rates of diffusion of chemical species into and out of the char particle. The rate of combustion of coal chars is an important parameter on combustion efficiency because of its impact on the unburnt carbon in the ash. Rationalization of the relationship between char reactivities in combustion and coal/char chemical and physical properties has therefore been attempted. In the chemical kinetic regime these include structural and chemical properties which increase the active surface area of the chars.

This paper considers the effect of some of these properties on porosity of coal chars and hence active surface area and reactivity. Particular emphasis will be placed on the following: (i) effect of devolatilisation conditions on porosity, (ii) effect of porosity on reactivity of coal chars and (iii) effect of mineral and heteroatoms content, and their distribution, on reactivity

Experimental methods

Coal chars were prepared from three British bituminous coals (70-90 μm), Markham Main (MM), Kiverton Park (KP), and Goldthorpe (G), by heating in an inert atmosphere to different heat-treatment temperatures (400-900 $^{\circ}\text{C}$) and at different heating rates (10 K/min (slow) or $1-10^4$ K/s (rapid)). The coal chars were characterized for their surface areas (N_2 and CO_2 adsorption at 77 or 195 K respectively), density, and porosity (mercury porosimetry). Chars were also examined by SEM. Isothermal char reactivities in air were measured in the temperature range 395-764 $^{\circ}\text{C}$ using a Beckman LM 600 microbalance.

Results and Discussion

The physical properties of the coal chars produced at slow pyrolysis are given in Table 1. For all three coals the surface area of the char is seen to pass through a minimum with increasing heat-treatment temperature. The surface areas measured by CO_2 adsorption are much higher than those measured by N_2 adsorption which is indicative of the presence of micropores which are

inaccessible at 77K due to activated diffusion. The density of the chars increase with increasing heat-treatment temperature, while the effect on porosity is more subtle.

The general trends in the changes in surface areas with heat-treatment can be explained in terms of the expected behavior for bituminous coals. At temperatures of between 200-500 °C the coals begin to soften and some volatile gases are evolved resulting in a loss of disordered material within the coal and an improvement in the stacking of the lamellae. A consequence of this is decreasing surface area. Upon further heating (500-600 °C), loss of tars begins resulting in swelling and an increase in the porosity (micro, meso and macro) hence both N₂ and CO₂ surface areas begin to increase again, as do the pore volume and porosity. At still higher temperatures (600-900 °C) resolidification of the coke structure occurs and the lamellae begin to grow with loss of H₂, resulting in increasing meso- and microporosity. These structural changes are validated by the spectroscopic properties and by elemental analysis of the chars. The role of N is also identified in this way.

The reactivity of coals in an oxygen atmosphere were obtained from experimental measurements. These apparent reactivities of the coals were converted into the values per unit surface area of the sample at one atmosphere oxygen partial pressure (i.e. the intrinsic reactivity R_i). The intrinsic reactivity, p_i, is used to normalize carbon reaction rates for differences in porosity:

$$p_i = R_i p_{O_2}^n \quad (1)$$

$$R_i = \frac{R_c}{A_g \gamma \sigma_a \eta} \quad (2)$$

Where R_i is the intrinsic reaction rate coefficient, P_{O₂} is the oxygen partial pressure, n the reaction order, A_g is the specific (pore) surface area, γ is the characteristic dimension of the particle, σ_a is the apparent density of the char and η is the effectiveness factor, calculated using Thiele's modulus in a unimodal pore system. The chemical rate coefficient, R_c, can be obtained from:

$$R_c = R_D p_{O_2}^{-(n-1)} \frac{X}{(1-X)^n} \quad (3)$$

where, R_D is the rate coefficient for oxygen diffusion to the particle, and X is the ratio of the actual burning rate to the maximum burning rate.

Figure 1 shows the Arrhenius plots of the R_i values not only for the coals examined in present study but includes values collected by the authors (1) for 6 different types of coal including petroleum coke. Figure 1 also includes values of intrinsic reactivity for 32 samples collected by Smith (2). Figure 1 shows R_i at a specific temperature ranging over up to two orders for the coal-types investigated. Values for the char activation-energies obtained from the intrinsic reaction rates were between 172 ± 12 kJ/mole and the pre-exponential factor was approximately 50 g/cm²s for the temperature ranges under investigation. As R_i is the reactivity per unit surface area of the coal, the differences in intrinsic reactivities must be attributed to other factors than porosity of the char sample. To clarify the relative importance of the other factors likely to affect the char oxidation process, relationships between R_i and some physical properties of the coals were examined.

Relationship between char reactivity and ash, H and carbon content: It is well established that overall coal reactivities are affected by the presence of minerals (3,4). The relationship between mineral matters and char reactivity R_i, is explored in (Figure 2). Although the number of coals studied during this investigation is very limited, it appears that reactivities R_i of the chars of higher rank coals are influenced by ash concentration. At low oxidation temperatures (<600 °C) the non-linear behavior of the R_i with ash concentration indicates that char reactivity may be controlled by the catalytic activity of coal minerals. However, at higher oxidation temperature (>600 °C) the intrinsic reactivity depends linearly on the char's ash content which may represent a non-catalytic reaction of carbon. Therefore, reduction in R_i with increasing ash content would be due to an inhibition of the carbon reactivity by the ash.

The relationship between R_i and hydrogen content of the coals is shown in Figure 3. The results imply a relationship very similar to the ash-char reactivity relationship. It is known that coal hydrogen content is directly related to the volatile content of the coal, and the number of carbon active sites on char can be related to the devolatilisation process and volatile concentration.

Therefore, the decrease in reactivity of char with hydrogen content can be related to the reduction in active sites.

Figure 4 shows the relationship between intrinsic reactivity and carbon content of the sample coals. At higher oxidation temperatures the intrinsic reactivity decreases monotonically with carbon content. Lower oxidation temperatures result in a optimum carbon concentration for maximum reactivity.

Reactivity and char structure: In a previous investigation by the authors (5), a correlated chemical reactivity is evaluated for 24 chars and cokes. The correlated chemical reactivity was based on all the chemical and physical variables of the coal. The resulting relationship is:

$$R_c = [1.4 (Vit_m + 0.83 Vit_{ps})] - 0.6(\ln_R + 1.6 \ln_{LR})] \exp^{(-.89)} \sigma_a^{(-.7.5)} Ag^{(-0.5)} C^{(3.5)} T_p^{(9.5)} \quad (4)$$

where \ln_R and \ln_{LR} are the fractions of low reflectance (reactive) and high reflectance (less reactive) inertinite respectively, and Vit_m and Vit_{ps} is the fraction of matrix and pseudo vitrinite respectively, C the carbon content and T_p the particle temperature.

The class of empirical formulations, of which equation 4 is an example, is of paramount importance to computational modelling. Other investigations have also produced a number of similar classes of formulations (6). Careful consideration of the results indicates that statistical analysis of char burn-out is necessary to describe the reactivity characteristic because of the complicated interplay of factors.

Conclusions

Values for the char activation-energies obtained from the intrinsic reaction rates were between $172 \pm 12 \text{ kJ/mole}$ for the temperature ranges under investigation. The current studies indicate strong interactions between carbon content, ash, and hydrogen content during the char-oxidation process. These interactions have been quantified for the coals studied.

References

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Table 1: Physical properties of Markham Main coal chars produced by slow pyrolysis

Char	HTT (°C)	Surface Area (m ² /g)		Density (g/cm ³)		Pore vol. (cm ³ /g)	Porosity (%)
		N ₂ @ 77K	CO ₂ @ 195 K	He	Hg		
MM-400	400	5.8	257.3	0.99	0.95	0.040	4.04
MM-500	500	0.7	113.7	1.01	0.98	0.030	2.97
MM-600	600	1.1	181.5	1.07	1.02	0.046	4.67
MM-700	700	3.6	179.7	1.15	1.07	0.065	6.96
MM-800	800	10.8	272.1	1.23	1.18	0.034	4.07
MM-900	900	11.3	210.0	1.46	1.33	0.067	8.90
KP-400	400	4.1	91.3	0.98	0.94	0.043	4.08
KP-500	500	0.4	73.1	0.99	0.96	0.032	3.03
KP-600	600	0.8	67.9	1.01	0.98	0.030	2.97
KP-700	700	5.6	221.7	1.03	1.01	0.020	1.94
KP-800	800	8.1	211.6	1.06	1.03	0.030	2.83
KP-900	900	9.6	184.4	1.19	1.12	0.050	5.88
G-400	400	3.6	48.3	1.05	0.95	0.100	9.52
G-500	500	0.3	49.9	1.01	0.97	0.040	3.96
G-600	600	0.2	29.1	1.08	1.01	0.064	6.48
G-700	700	0.9	262.6	1.11	1.09	0.016	1.80
G-800	800	5.9	215.1	1.13	1.10	0.024	2.65
G-900	900	5.1	-	1.27	1.19	0.053	6.30

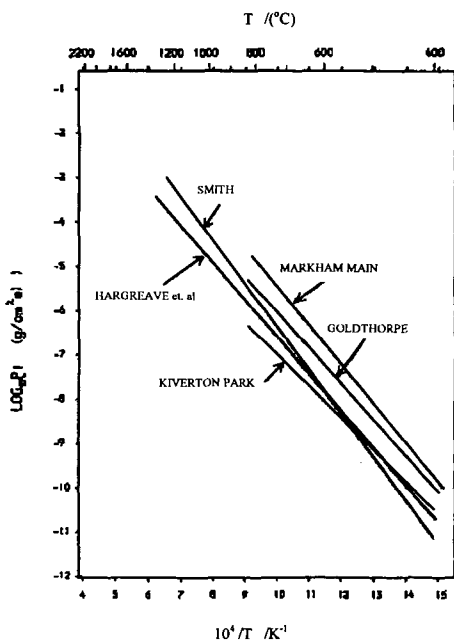


Figure 1: Comparison of Intrinsic chars reactivity in air

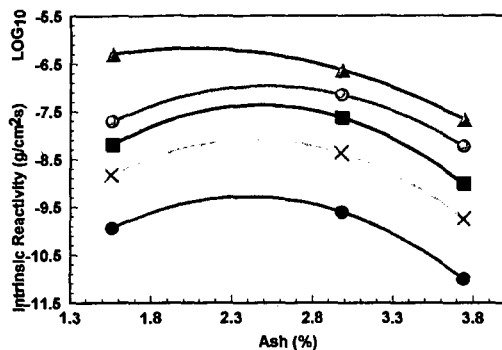


Figure 2: Relationship between Intrinsic reactivity and % ash in char. Oxidation temperature Δ 900C, \circ 800C, \blacksquare 700C, \times 600C and \bullet 500C.

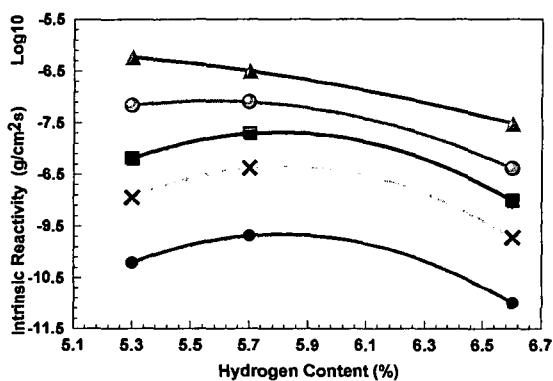


Figure 3. Relationship between Intrinsic reactivity and H in coal samples. Symbols as in Fig. 2.

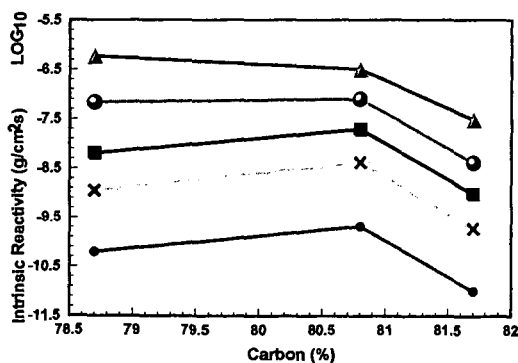


Figure 4: Relationship between intrinsic reactivity and %carbon of the char. Symbols as in Fig. 2.